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ULTRAMICRO NANOMETER ELECTRODE AND ULTRAMICRO SENSOR

Xueji Zhang et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
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ULTRA MICRO NANOMETER ELECTRODE AND ULTRAMICRO SENSOR

[Nami ji chao wei dian ji ji chao wei chung gan gi]

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Inventors:	Xueji Zhang, et al.

Number of the pages of the description:	2
Number of the pages of the attached figures:	2

Claims

1. A method of making up the nm-class ultramicro electrode using the ion beam etching technique and making up the ultramicro sensor by trimming the surface of the nm-class electrode, and characterized by that through bombardment of the tip of the nm-class micro carbon fiber and metal ultramicro electrode with the ion beam, the nm-class electrode tip is prepared, and on the surface of the nm-class column electrode prepared a nm-class insulating layer of 3-allyl o-dihydroxy benzene is voltolized. Then the tip of the electrode is cut open so that its plane is exposed, to become a nm-class disk electrode, and through trimming of polyaniline on the surface of the nm-class electrode, the pH sensor is prepared; finally the nm-class electrode prepared is bonded with the electrode supporter and the electrode material in a vacuum; and the minimal diameter of the electrode prepared can reach 30 nm.

2. The nm-class electrode as described in Claim 1, characterized by that for bombardment of the carbon fiber or metal tip by the ion beam, the parameters selected for the ion beam are: accelerating voltage $V_a \leq 2000$ to 8000 KV, the ion beam current ≥0.1 to 20 mA, the glancing angle $\beta \geq 10$ to 35°C, the rotating target speed $\omega \geq 5$ to 85 rpm, the bombardment time t ≥2 to 20 hr, the vacuum degree $\tau \geq 0.0001$ to 0.005 Pa;

3. The insulating layer on the surface of the nm-class electrode as described in Claim 1, characterized by that the composition of the voltolized electrolyte is 3-alkyl o-dihydroxy benzene: ≥0.05 to 0.2 mol/L, phenol ≥ 1.0×10^{-6} to 1.0×10^{-4} mol/L, butanol ≥0.1 to 0.5 mol/L, and they are dissolved in the aqueous solution of methanol ≥ 20 to 80%, and adjusted with $NH_3 \cdot H_2O$ until the pH value reaches the range ≥ 8.5 to 10.0; potential for polymerization: ≥ 3.0 to 4.0 V; polymerization time: ≥ 5 to 15 min; cross-linking temperature: ≥ 120 to 250°C; cross-linking time: ≥ 10 to 30 min.

4. The nm-class electrode as described in Claims 1 and 2, characterized by that through heating in a vacuum, the supporter glass capillary and the carbon fiber or metal electrode material are sealed together.

Description of the invention

Disclosed in the present invention is the method of preparing a nm-class ultramicro electrode and an ultramicro sensor. It falls into the technical fields of analytical chemical, electroanalytical chemical, and electrochemical sensors.

There has not been much development in the researches of nm-class ultramicro electrodes, and this is mainly due to the fact that the technique for preparing nm-class ultramicro electrodes is highly difficult, and even when nm-class ultramicro electrodes are prepared, due to various reasons, most of them are actually not practical. A method of preparing the nm-class platinum band electrode was reported by White et al; (H.S.White et. al. J. Phys. Chem., 1987, 91,3559), and we (ZHANG Xueji, ZHANG Wuming, ZHOU Xingyao, WANG Zhu <<Gao Deng Xue Xiao Hua Xue Xue Bao (Journal of Chemistry of Chinese Universities and Colleges)>>1993, 14 (7) 927) made an exhaustive study of the preparation and characteristics of nm-class gold band electrodes. Penner et al (R.N. Penner et al., Sci., 1990, 250, 1180) suggested that the method of heated drawing be used to prepare nm-class platinum disk electrodes. With the work mentioned above, a certain foundation has been laid for theoretical studies of nm-class electrodes. However, although electrodes mentioned above are known as nm-class electrodes, the size of the whole electrode is relatively large, and the electrode is buried in a large supporter, and is not applicable to micro zone analysis, thus extremely limiting the application of the electrode. Besides, with some processing technologies (such as the method of heated drawing) it is very difficult to guarantee the repeatability of the electrode. Recently, Ewing et al. (A.G. Ewing et. al,

Anal. Chem., 1992, 64. 1368) etched carbon fiber in the flame, and prepared the nm-class carbon fiber electrode (with the diameter at the tip around 400 nm or so), thus making a step forward in the application of nm-class electrodes to the micro zone. Yet the rate of success of making the electrode using this method is low, and it is impossible to make the same electrode. The electrode prepared using this method has a rough surface, and poor strength, and it is neither appropriate for theoretical studies, nor really applicable to actual use. Particularly in the aspect of application to substance analysis inside cells, this kind of electrode is even more helpless.

The purpose of the present invention is: to prepare a nm-class ultramicro carbon fiber electrode and other metal ultramicro electrodes featuring controllable size, smooth surface, high mechanical strength, and good eletrochemical performance, using the ion beam etching technique; suggesting voltolization of a 3-allyl o-dihydroxy benzene nm-class insulating layer on the surface of the nm-class column electrode prepared; and then preparation of the nm-class disk electrode using the method of cutting open the tip of the electrode so that the plane is exposed. For the first time a pH sensor is prepared by means of trimming aniline on the surface of the nm-class electrode.

Technical measures adopted to accomplish the purpose of the present invention include:

1. Bombardment of the tip of the carbon fiber with the ion beam to prepare the nm-class electrode tip. During the bombardment, the experimental parameters are: accelerating voltage V_a = 2000 - 8000 kV, the ion beam current I = 0.1 - 20 mA, the glancing [grazing] angle θ = 10 – 35°C, the rotating target speed ω = 5-85 rpm, the bombardment time t = 2-20 hr, the vacuum degree τ = 0.05-0.0001 Pa.

2. The carbon fiber is connected with the coaxial shielding wire with silver powder electroconductive resin, and after connection, it is placed at 60-80°C for 0.5-2 hr.

3. By means of heating under a vacuum, the supporter glass capillary is sealed together with the carbon fiber or metal electrode, thus avoiding contamination of the surface of the electrode.

4. The method of voltolization of 3-allyl o-dihydroxy benzene is used for insulation. The experimental conditions are: composition of the electrolyte is 3-allkyl o-dihydroxy benzene of 0.05-0.2 mol/L, phenol of 1.0×10^{-4}-1.0×10^{-6} mol/L and butanol of 0.1-0.5 mol/L, and dissolved in an aqueous solution of methanol of 20-80%, and adjusted with NH_3 H_2O until the pH value reaches the range of 8.5-10.0. Potential for polymerization: 3.0-4.0 V; polymerization time: 5-15 min; cross-linking temperature: 120-250°C; cross-linking time: 10-30 min.

The nm-class electrode prepared using the present invention has the following advantages: 1. The size of the electrode prepared is controllable, and the minimal effective tip can be prepared up to 30 nm. 2. As atoms on the surface of the carbon fiber are "knocked" off one after the other, the surface of the carbon fiber has the molecule-class flatness and

smoothness, the carbon fiber gets thicker homogeneously like a needle from the tip backward, and the electrode prepared has a very clean surface and high strength. Therefore the electrode has excellent electrochemical performance, and it can be easily inserted into a single cell for measuring. Entering the cell requires that the electrode have a high strength and a smooth surface; in this way, sealing is easier between the cell membrane and the electrode. 3. A high rate of success. Because of the use of ion beam etching, various parameters can be put under strict control, thus ruling out factors such as artificial "skills" in the method of flame etching. 4. Good reproducibility of the electrode. So far as the controlling parameters are consistent, electrodes of the same parameters can be obtained. 5. Batch production. A critical step forward for commercialization of the nm-class electrode and the nm-class sensor.

The electrode prepared has been successfully inserted for the first time into a single nerve cell only 10 μm in diameter, and a dynamic analysis was made. In March 1994, an appraisement was made of this project by the National Committee of Education, who believed that the isoion beam etching technique which was used for the first time in preparation of the carbon fiber ultramicro electrode and the nm-class carbon fiber ultramicro electrode prepared, was taking the lead internationally. And the said electrode was also successfully inserted to the single nerve cell for testing, and making it a significant breakthrough. Therefore, the said achievement is on the internationally advanced level.

About the attached drawings: Figure 1 is a schematic diagram of the electrode. 1 in Figure 1 is the carbon fiber; 2 is the insulating layer; 3 is the electrode tip; 4 is the plane where the carbon fiber in the electrode is bonded with the glass tip capillary; 5 is the connecting point of the carbon fiber and the lead; 6 is the glass capillary, 7 is the lead, and 8 is the epoxy resin. Figure 2 is an electromicroscopic photograph of the electrode prepared using the present invention. Figure 3 is the electromicroscopic photograph of the electrode prepared using the flame method.

Example of the application: The carbon fiber with the surface cleaned, and 7 μm in diameter, is connected with the wire using the silver powder electroconductive resin. At 70°C, it is placed for 1 hr, and under the microscope it is inserted through a capillary which has been pulled and prepared (the tip is 10 μm in diameter) with around 10-100 μm of the carbon fiber exposed. On the back, the wire and the capillary are fixed with epoxy resin, and in a vacuum, the tip of the capillary is heated, sealed and melted, and in the ion beam current the tip of the carbon fiber is etched to nm class, and the specific parameters Va = 4000 kV; I = 5 mA; θ = 15°C, ω = 10 rpm, t = 10h, τ = 0.0005 Pa and the nm-class column electrode is prepared.

The electrode mentioned above, with the polymerization potential V = 3.5 V, polymerization time t = 10 min, composition of the electrolyte is: 0.1 mol/L 3-allyl o-dihydroxy benzene, phenol of 100 x 10^{-5} mol/L, butanol of 0.15 mol/L, and solvent being 1:1 aqueous

solution of methanol, is adjusted with ammonia water until pH = 9.2, and the nm-class polymeric membrane is obtained. The said electrode is put to ultrasonic rinsing for 5 min with secondary water, and ethanol respectively, and cross-linked at 140°C for 20 min, and then in the microscopic operating system a little bit of the tip of the electrode is cut off so that the nm-class disk electrode is exposed.

DRAWINGS ATTACHED TO THE DESCRIPTION

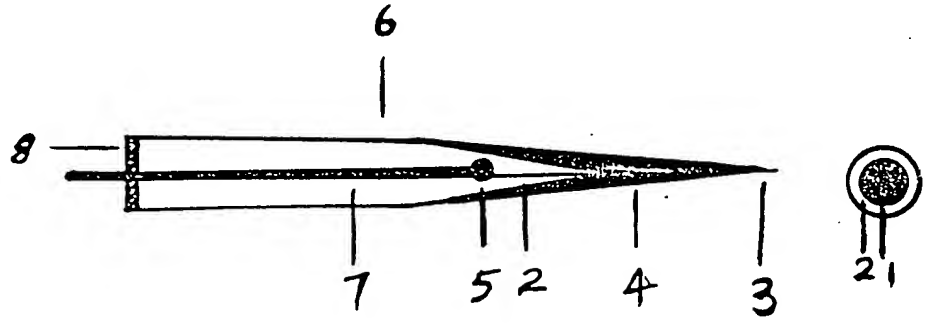

Figure 1. A schematic diagram of the electrode

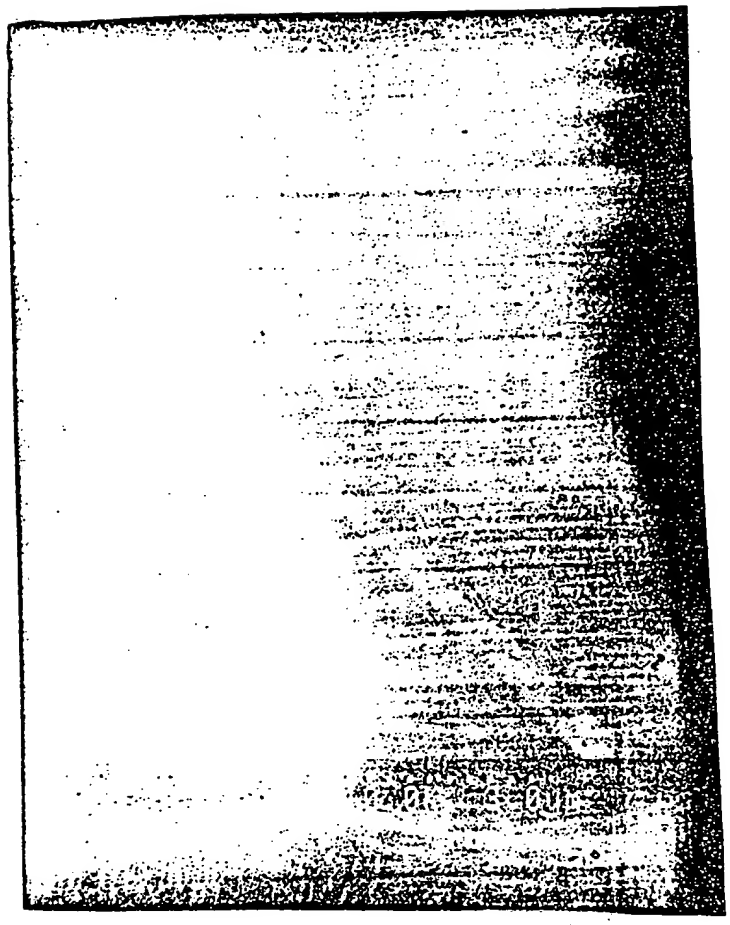

Figure 2. An electromicroscopic photograph of the electrode prepared using the present invention

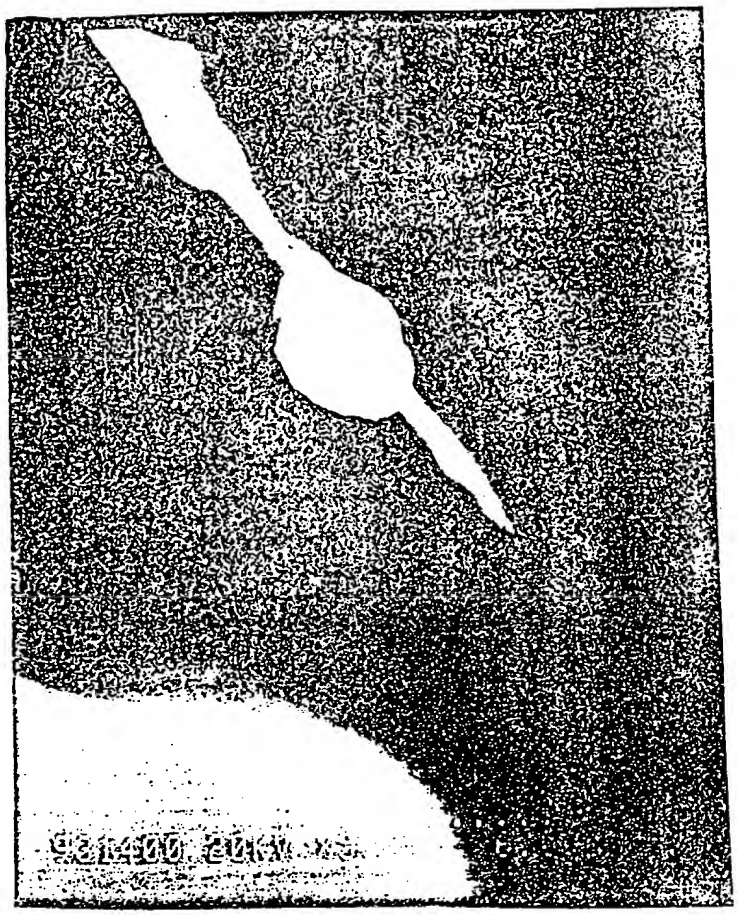

Figure 3. An electromicroscopic photograph of the electrode prepared using the flame method